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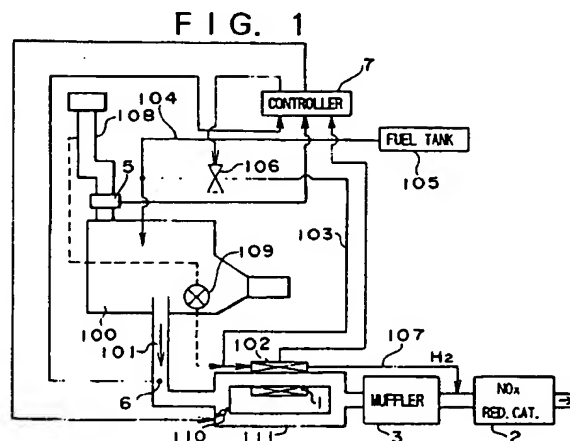
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54 Nitrogen oxides decreasing apparatus for an internal combustion engine.

57 A lean NO_x reduction catalyst (2) capable of reducing NO_x through reaction of H₂ with NO_x at low temperatures below 350°C is installed in a downstream portion of an exhaust pipe (101) of an internal combustion engine (100) in or near a muffler (3). Such an NO_x reduction catalyst (2) comprises, for example, Pt/zeolite catalyst. An H₂ generator (102) is installed so as to supply the H₂ to an inlet side of the NO_x reduction catalyst (2). The H₂ generator (102) may include a reforming catalyst (1) for reforming methanol, LPG, or natural gas to generate H₂. The generated H₂ flows to the NO_x reduction catalyst (2) where it reacts with NO_x to purify the exhaust gas.



where the methanol or hydrocarbons are reformed to generate H_2 . The generated H_2 is supplied into the exhaust conduit of the engine at the inlet side of the NOx reduction catalyst and is mixed with NOx-containing exhaust gas from the engine. The NOx reduction catalyst causes H_2 and NOx to react with each other at low temperatures to reduce NOx. Since NOx is reduced through reaction with H_2 independently of a concentration of O_2 included in exhaust gas, the air-fuel ratio can be freely determined from the viewpoint of good combustion and fuel economy without having to achieve minimum generation of NOx. As a result, a high fuel economy and good driveability can be maintained.

The above-described object and other objects, features, and advantages of the present invention will become more apparent and will be more readily appreciated from the following detailed description of the preferred embodiments of the invention taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a schematic system diagram illustrating a basic arrangement of an NOx decreasing apparatus for an internal combustion engine in accordance with the present invention;

FIG. 2 is a graphical representation of a specific fuel consumption versus air-fuel ratio characteristic;

FIG. 3 is a graphical representation of an NOx and specific fuel consumption versus air-fuel ratio characteristic;

FIG. 4 is a graphical representation of an NOx conversion versus inlet gas temperature characteristic;

FIG. 5 is a graphical representation of an NOx conversion versus ratio of amount of supplied H_2 to amount of NOx characteristic;

FIG. 6 is a schematic system diagram of an apparatus in accordance with a first embodiment of the invention;

FIG. 7 is an enlarged cross-sectional view of an H_2 generator of the apparatus of FIG. 6;

FIG. 8 is a still further enlarged cross-sectional view of an inlet end portion of the H_2 generator of FIG. 7;

FIG. 9 is a schematic system diagram of an apparatus in accordance with a second embodiment of the invention;

FIG. 10 is an enlarged side view of one embodiment of an H_2 mixer and NOx reduction catalytic converter according to the invention;

FIG. 11 is a graphical representation comparing NOx converting characteristics of a pellet-type catalyst and a monolithic catalyst used in the NOx reduction catalytic converter of FIG. 10;

FIG. 12 is a partial cross-sectional view of a pellet-type catalyst for use in the NOx reduction catalytic converter of FIG. 10;

FIG. 13 is a partial cross-sectional view of a monolithic catalyst for use in the NOx reduction catalyst container of FIG. 10;

FIG. 14 is a further enlarged cross-sectional view of an H_2 mixer for use in the apparatus of FIG. 10;

FIG. 15 is a cross-sectional view of the mixer taken along line 15-15 of FIG. 14;

FIG. 16 is a schematic cross-section illustrating a dimensional relationship between a diameter d of an H_2 injection nozzle and a diameter D of an exhaust conduit in the apparatus of FIG. 14;

FIG. 17 is a cross-sectional view of another mixer for use in the apparatus of FIG. 10;

FIG. 18 is a cross-sectional view of the mixer taken along line 18-18 of FIG. 17;

FIG. 19 is a graphical representation of an NOx conversion versus inlet gas temperature characteristic of an apparatus in accordance with a fourth embodiment of the invention;

FIG. 20 is an enlarged partial cross-sectional view of another embodiment of an H_2 mixer and NOx reduction catalytic converter according to the invention;

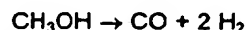
FIG. 21 is a cross-sectional view of the apparatus of the embodiment of FIG. 20 taken along line 21-21; and

FIG. 22 is a partial cross-sectional view of still another embodiment of an H_2 mixer and NOx reduction catalytic converter according to the invention.

With reference to FIG. 1, in an NOx decreasing apparatus for an internal combustion engine in accordance with the present invention, an H_2 generator 102 for generating H_2 and supplying the generated H_2 to an exhaust conduit 101 of an engine 100 includes a reforming catalytic converter 102 containing a reforming catalyst 1. The type of reforming catalyst 1 is selected according to the kind of fuel used in the engine.

More particularly, in an engine using methanol as fuel, the following three types of reforming catalysts can be used:

(1) At least one metal selected from the group consisting of noble metals such as palladium (Pd) and platinum (Pt), and transition metals such as copper (Cu), chrome (Cr), and nickel (Ni), is used as catalyst metal of the reforming catalyst. Methanol is evaporated by heat of the exhaust gas and is reformed at the reforming catalyst to generate H_2 . The temperature of an inlet portion of the reforming catalyst is maintained at about 300°C. The reaction at the reforming catalyst is as follows:



(2) A Cu-Ni-Cr/alumina catalyst (Cu-Ni-Cr is deposited onto a carrier of alumina) is used as the reforming catalyst. Methanol fuel is evaporated

air control valve 109.

FIG. 5 shows curves of NOx conversion versus ratio of H₂ to NOx. When H₂ is supplied at the ratio that H₂ : NOx = 2 : 1, all NOx will be reduced as shown by the theoretical line in FIG. 5, if the NOx and the supplied H₂ react completely with each other. However, since NOx and H₂ will not react completely with each other, the actual conversion will be as shown by the experimental curve in FIG. 5. At H₂/NOx ratio less than 2.0, the experimental curve is positioned to the left of the theoretical line. This is because water vapor included in the exhaust gas is transformed into H₂ on the noble metal-type catalyst. Thus, more H₂ than the amount supplied from the reforming catalytic converter is available to react with the NOx.

In one embodiment of the invention, a mixer for mixing the supplied H₂ with exhaust gas may be installed on an inlet side of the NOx reduction catalyst. In another embodiment of the invention, the reforming catalytic converter is installed downstream of an oxidation catalyst disposed at an outlet of an exhaust manifold of the engine, and the NOx reduction catalyst is installed in or downstream of the muffler so that the catalysts are maintained at respective optimum temperatures.

In yet another embodiment of the invention, an HC oxidation device for oxidizing HC and CO, such as an oxidation catalyst, a three-way catalyst, and an exhaust reactor is installed in a portion of the exhaust conduit close to the exhaust manifold, and Pt-zeolite catalyst (where Pt is deposited on zeolite) is used as the lean NOx catalyst. Further, the NOx reduction catalytic converter and the exhaust muffler are integrally constructed into a single assembly in which the NOx reduction catalyst is provided with a muffler function.

Further, in a diesel engine, a soot trapper or an unburned HC oxidizing device may be provided upstream of the NOx reduction catalyst. Furthermore, the present invention may be applied not only to a lean burn gasoline engine and a diesel engine but also to a hydrogen engine where hydrogen gas is used as fuel. In the case of a hydrogen engine, an H₂ generator is not required and a portion of the H₂ fuel can be supplied to an inlet side of the NOx reduction catalyst.

These embodiments of the invention will be explained in more detail below.

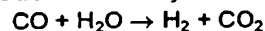
FIG. 6 illustrates a first embodiment of the invention where the system of the invention is applied to a lean burn gasoline engine 112 with an engine displacement of 1 liter. The engine 112 of the first embodiment is operated at excess air ratios of 0.95 - 1.0 (slightly rich or just a stoichiometric air-fuel ratio) in an idling condition, at excess air ratios of 0.8 - 1.0 (rich) in a full load condition and a rapid acceleration condition, and at excess air ratios of 1.2 - 1.8 in the remaining engine operating conditions. An oxidation

catalyst 9 is installed in an exhaust conduit 113 near an outlet of an exhaust manifold 8 to oxidize unburned products such as HC and CO. Further, an NOx reduction catalyst 12 is disposed in the exhaust conduit downstream of a muffler 13. A mixer 10 is provided on the inlet side of the reduction catalyst 12 to evenly mix H₂ with exhaust gas.

An H₂ generator 11 (shown in enlarged detail in FIG. 7) includes an inner core in the form of a coiled tube 114 inserted in the exhaust conduit. At an inlet end 114a of the inner core, an electromagnetic fuel injection valve 115 is provided for injecting methanol fuel into the inner core. An outlet end 114b of the inner core leads to the mixer 10 through a conduit 116. As shown in FIG. 8, a porous ceramic member 117 for evaporating the methanol is located at the inlet of the inner core, and a reforming catalyst 14 in the form of pellets fills the inner core downstream of the methanol evaporating ceramic member. If the reforming catalyst is in monolithic form, the inner core is changed from a coil to a straight tube. Pd is used for the reforming catalyst.

In FIG. 6, an intake air sensor 15 is installed in the intake conduit 118 to detect the amount of air supplied to the engine 112, and an NOx sensor 16 is installed in the exhaust conduit of the engine to detect the NOx concentration of the exhaust gas. In the one-liter engine example of FIG. 6, since the moles of H₂ required are equal to the moles of NOx, 0.3 l/min of H₂ is necessary at a vehicle speed of 50 Km/h and 1.0 l/min of H₂ is necessary when the engine is operated at the maximum output. The H₂ is produced by reforming a portion of the fuel. The portion of fuel consumed to produce the required H₂ is equal to or less than 1 - 2% of the fuel required to drive a vehicle. As an amount of 15 - 20% of fuel is saved by using a lean burn engine, the amount of 1 - 2% is negligible compared with the amount of 15 - 20%. Thus, the fuel economy of the lean burn engine is not degraded by adding an H₂ generator. In this connection, the amount of methanol required to generate the H₂ is about 0.15 l/min at a vehicle speed of 50 Km/h.

In the first embodiment of the invention, since only a small amount of fuel is reformed by the H₂ generator 11 and NOx is reduced through reaction with the generated H₂ at the NOx reduction catalyst 12 at low temperatures, the amount of NOx can be decreased independently of the excess air ratio of the engine 112. CO, which may be produced together with H₂, can be transformed by the following reaction:



Further, CO can be separated from H₂ by a Pd membrane, and H₂ of high purity can be supplied into the inlet side of the NOx reduction catalyst 12. However, since the amount of produced CO is very small, CO acts as a reduction material in the NOx reduction catalyst 12. Thus, there is no fear that CO is exhausted to atmosphere.

monolithic NOx reduction catalyst.

For example, the effect of the mixer was evaluated using a lean burn gasoline engine of 1.6 liters. In the tests, the engine speed was 2000 rpm, the torque was 40 Nm, and the NOx exhaust amount was 0.44 l/min. Without an H₂ mixer, the H₂ amount required to purify the NOx was 0.661 min, and the amount of fuel (methanol) to generate the H₂ was 0.33 l/min.

When the mixer of FIGS 17 and 18 with the ratio D/d of 2 was used, the amount of H₂ was 0.44 l/min, and the amount of fuel to generate the H₂ was 0.22 l/min. Therefore, the amount of 0.11 l/min of fuel could be saved as compared with the above-described case having no mixer.

FIGS. 20 and 21 illustrate another embodiment of an H₂ mixer and NOx catalytic converter wherein a lean NOx catalyst 82 is disposed in a muffler 80. When the NOx reduction catalyst is disposed in or near a muffler, where the exhaust gas temperature is low, the reaction rate of H₂ with NOx is not high. So, the NOx reduction catalyst should be used at SV values (a ratio of the volume of exhaust gas passing through the catalyst to the volume of the catalyst) of 10,000 - 60,000, which are smaller than the SV values of 50,000 - 100,000 of the conventional catalyst disposed near the exhaust manifold. This means that the required volume of the NOx reduction catalyst becomes greater than that of the conventional catalyst disposed near the exhaust manifold.

To make installation of the NOx reduction catalyst easy, the NOx reduction catalyst 82 and the muffler 80 are integrated as a single assembly 83 in the embodiment of FIGS. 20 and 21, wherein the lean NOx catalyst 82 is disposed in the exhaust muffler 80 so that the assembly 83 of the NOx reduction catalyst (Pt-zeolite catalyst) and the exhaust muffler is made compact.

Exhaust gas mixed with H₂ flows to the integral assembly 83 of the catalyst and muffler. The exhaust gas mixed with H₂ collides with a mixing plate 84 which has many apertures 85 of different sizes. When the exhaust gas mixed with H₂ flows through the apertures 85, the exhaust gas and H₂ mix well with each other. Then the mixed gas flows to the monolithic catalyst 82. Since no aperture is provided at a center portion of the mixing plate 84, the exhaust gas will not concentrate in a central portion of the monolithic catalyst 82. Since the sizes of the apertures 85 are different from each other, the speeds of portions of gas passing through the apertures are different so that the portions of gas are agitated and the sound is muffled due to interference between portions of the gas.

Since the muffler is usually disposed at a tail pipe of the exhaust conduit and the exhaust gas has been cooled before flowing to the muffler, the temperature of the gas entering the muffler is about 150

- 200°C at the maximum, and about 100 - 150°C in normal operations.

In the cases of the conventional three-way catalyst and the conventional Cu/zeolite-type lean NOx catalyst reducing NOx in the presence of HC, since these catalysts can show activity only in a temperature range above 300 - 400°C, they are not allowed to be disposed in a tailpipe muffler. As discussed above, however, when NOx reduction is effected by H₂ instead of by HC, NOx purification at low temperatures is possible. However, even in those cases, the temperature is in the range of 150 - 300°C and is slightly higher than the inlet temperature of the exhaust muffler.

It was experimentally investigated from the viewpoint of catalyst activity what kinds of catalysts should be used. From the experiments, it was found that Pd and Rh showed no activity, Cu showed a low activity, and Pt showed a high activity to reduce NOx in cooperation with H₂. However, it was also found that Pt should be highly distributed and that, for the high distribution, a carrier having a high specific surface area (greater than 100 m²/g) such as alumina, silica, or zeolite was necessary.

Further, it was investigated whether the exhaust gas should be pretreated before mixing with H₂. The experiment results are shown in FIG. 19. More particularly, when exhaust gas with no pretreatment was mixed with H₂ and the mixture was then introduced to the lean NOx catalyst (Pt catalyst), the lean NOx catalyst exhibited its peak activity at about 250°C, as shown by characteristic curve B in FIG. 19. On the other hand, if an oxidizing device such as an afterburner, a reactor, a three-way catalyst, or an oxidation catalyst was installed in the vicinity of the engine exhaust manifold, when exhaust gas was caused to flow through the oxidizing device so that CO and HC were removed from the exhaust gas, the lean NOx catalyst showed its peak activity at 100 - 150°C, as shown by characteristic curve A in FIG. 19.

This temperature range of 100 - 150°C coincides with the inlet temperature of the exhaust muffler, which means that it is possible to install the Pt/zeolite-type NOx reduction catalyst 80 within the exhaust muffler 80. Further, it was found that it would be better to remove HC and CO from the exhaust gas before the exhaust gas reached the NOx reduction catalyst. This is because NOx conversion by the lean NOx catalyst would be improved if no soot resulting from incomplete burning of HC were formed on the catalyst.

Further, the sound muffling effect is improved by installing an interference tube EX1 at a location downstream of the monolithic converter 82.

An H₂ mixing and NOx reduction catalytic converter apparatus of FIG. 22 is different from the apparatus of FIGS. 20 and 21 only in the structure of the mixer. More particularly, the mixer of FIG. 22 comprises a mixing pipe 86 having a plurality of apertures 85,

a mixer (10) for mixing H₂ with exhaust gas from the engine, the mixer (10) being located in the exhaust conduit at an inlet side of the NOx reduction catalyst (2, 12).

13. An apparatus according to claim 1, further comprising an oxidizing device (9) located in the exhaust gas conduit upstream of the NOx reduction catalyst for oxidizing HC and CO included in exhaust gas from the engine, and wherein the engine has an exhaust manifold having an outlet, the H₂ generator (11) being disposed at the outlet of the exhaust manifold, and the NOx reduction catalyst (12) being located in the muffler or a portion of the exhaust conduit downstream of the muffler (13).
14. An apparatus according to claim 1, further comprising an oxidizing device (9) for oxidizing HC and CO included in exhaust gas from the engine, and wherein the NOx reduction catalyst (12) is a Pt type catalyst which comprises platinum deposited on a carrier selected from the group consisting of zeolite, silica, and alumina.
15. An apparatus according to claim 14, wherein the Pt type catalyst of the NOx reduction catalyst (82) is housed in the muffler (80) to constitute a single assembly of the NOx reduction catalyst and the muffler.
16. An apparatus according to claim 1, wherein the H₂ generator (102) includes an inner core constructed of a coiled tube (114) inserted in the exhaust conduit, an electro-magnetic injection valve (115) for injecting methanol into one end portion, and a reforming catalyst (14) housed in the inner core and including Pd.
17. An apparatus according to claim 1, wherein the NOx reduction catalyst (2) comprises a pellet type catalyst (61).
18. An apparatus according to claim 12, wherein the NOx reduction catalyst (2) comprises a monolithic type catalyst (62), and wherein the mixer (10, 69) comprises an injection nozzle (63) connected to the H₂ generator and having a plurality of radially directed holes (64) for injecting H₂ there-through.
19. An apparatus according to claim 18, wherein the injection nozzle (63) has an outside diameter equal to or greater than 20% of an inside diameter of the exhaust conduit (65), the exhaust conduit being enlarged in diameter at a portion in which the injection nozzle is disposed, the injection nozzle (63) being spaced apart from the NOx re-

duction catalyst (60) by a distance at least twice the inside diameter of the exhaust conduit (65) and no more than ten times the inside diameter of the exhaust conduit (65).

20. An apparatus according to claim 12, wherein the NOx reduction catalyst (2) comprises a monolithic type catalyst (62), and wherein the mixer (10) comprises an injection nozzle (66) having a first diameter, and a cylinder (68) coaxial with and downstream of the injection nozzle (66), the cylinder (68) having a second diameter greater than the first diameter and having a plurality of injection apertures (67) formed in a wall of the cylinder.
21. An apparatus according to claim 20, wherein a ratio of the second diameter to the first diameter is in the range of 1.7 to 3.
22. An apparatus according to claim 21, wherein the ratio of the second diameter to the first diameter is substantially 2.
23. An apparatus according to claim 15, further comprising a mixing plate (84) disposed in the muffler (80) and upstream of the NOx reduction catalyst (82), the mixing plate (84) comprising a plate having apertures (85) of different sizes.
24. An apparatus according to claim 15, wherein the means for supplying the generated H₂ comprises a mixing pipe (86) disposed in the muffler and connected to the exhaust conduit, the mixing pipe (86) having apertures (85) formed in a wall of the mixing pipe (86), the H₂ generator injecting the generated H₂ into the mixing pipe (86).
25. An apparatus according to claim 14, wherein the oxidizing device is any one of an afterburner, a reactor, a three-way catalyst, and an oxidation catalyst.

FIG. 3

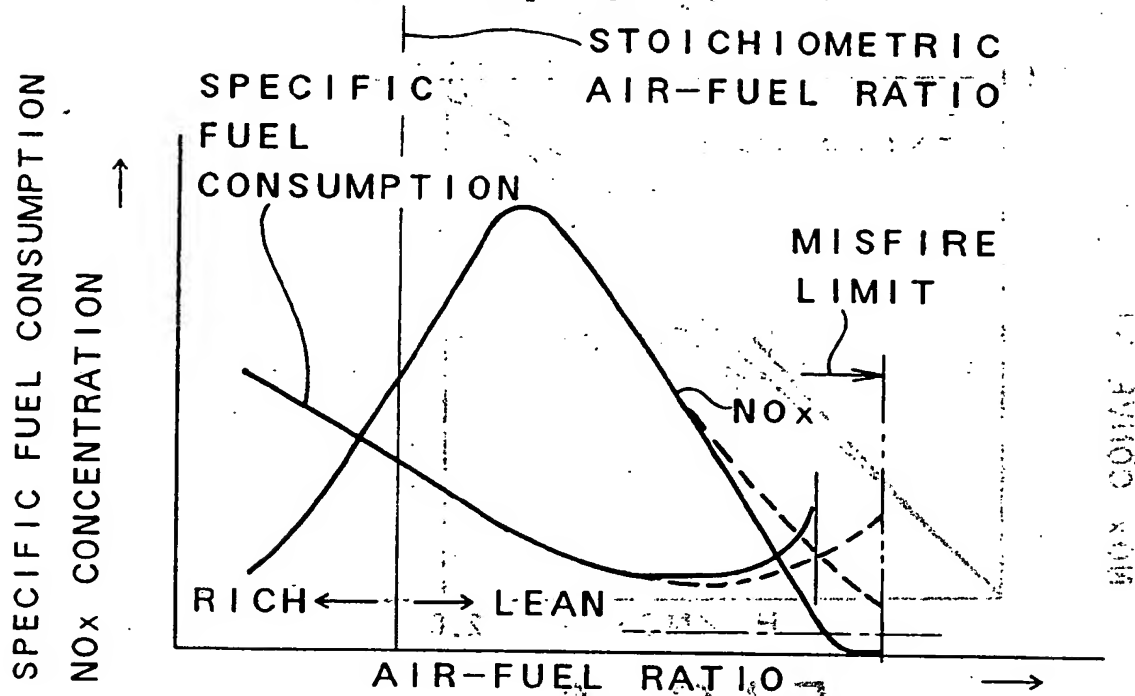


FIG. 4

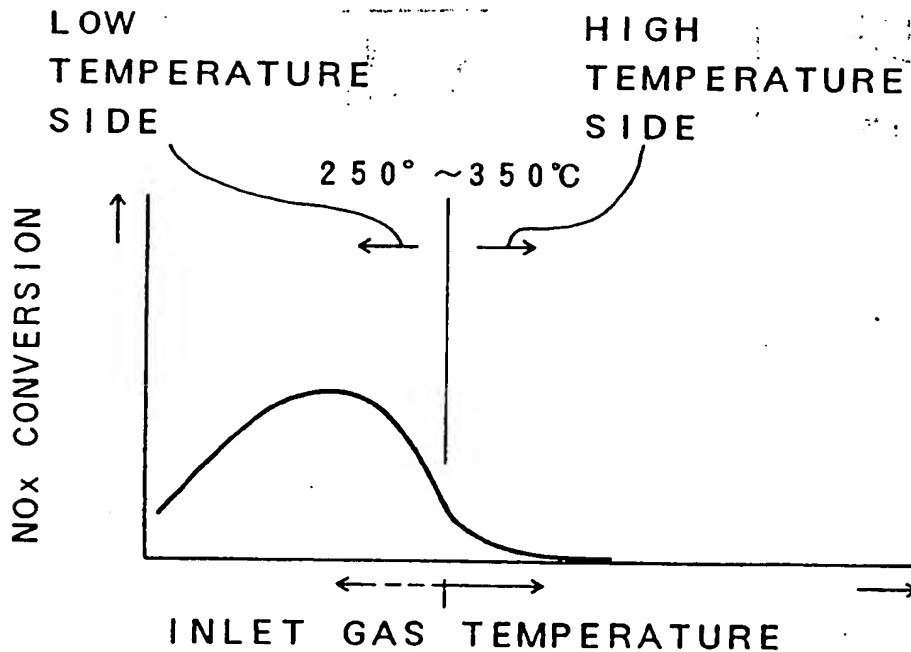


FIG. 7

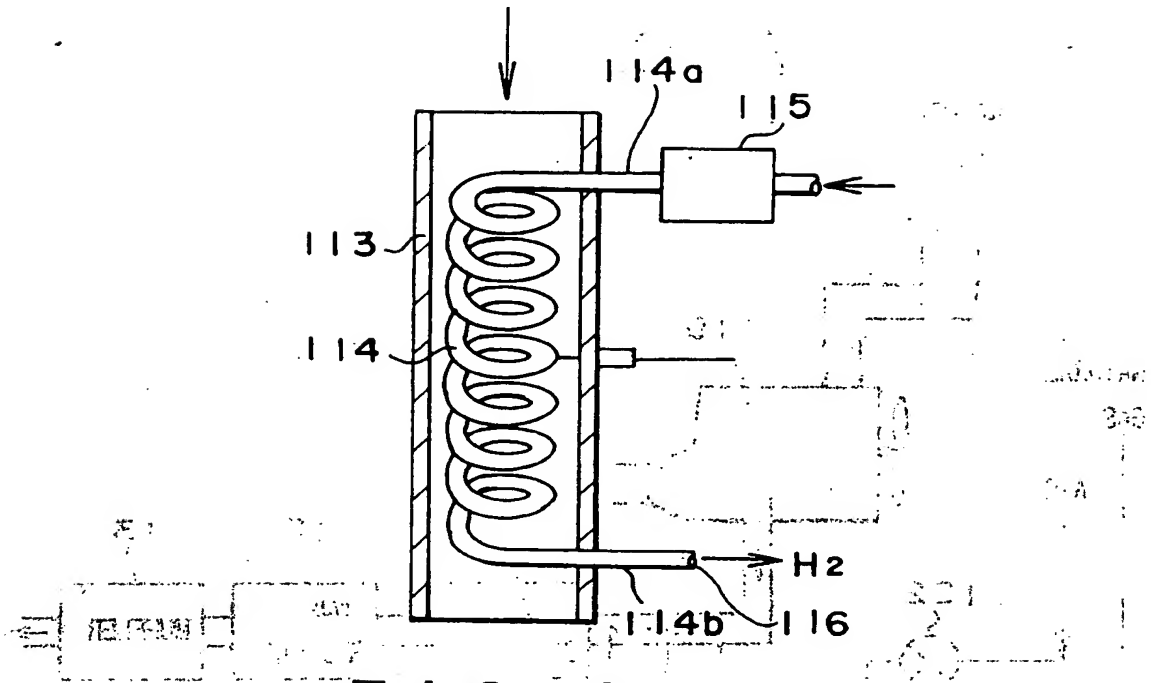


FIG. 8

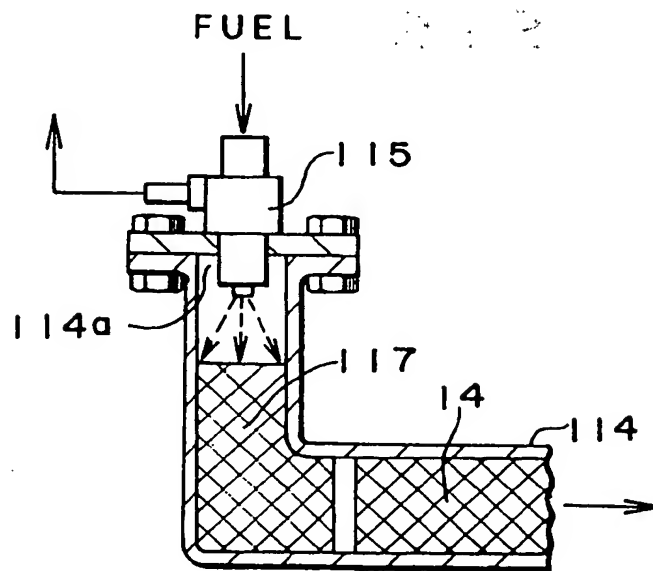


FIG. 11

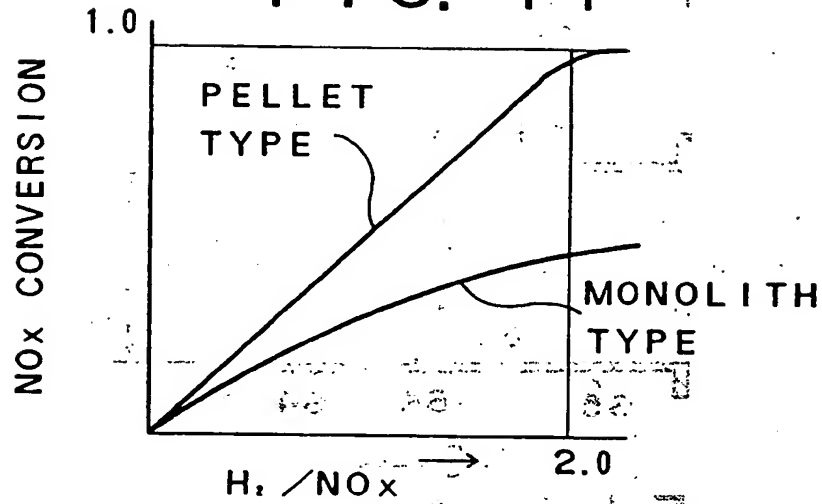


FIG. 12



FIG. 13

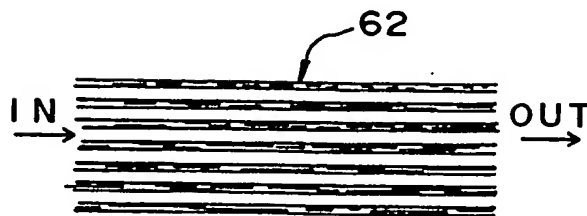


FIG. 17

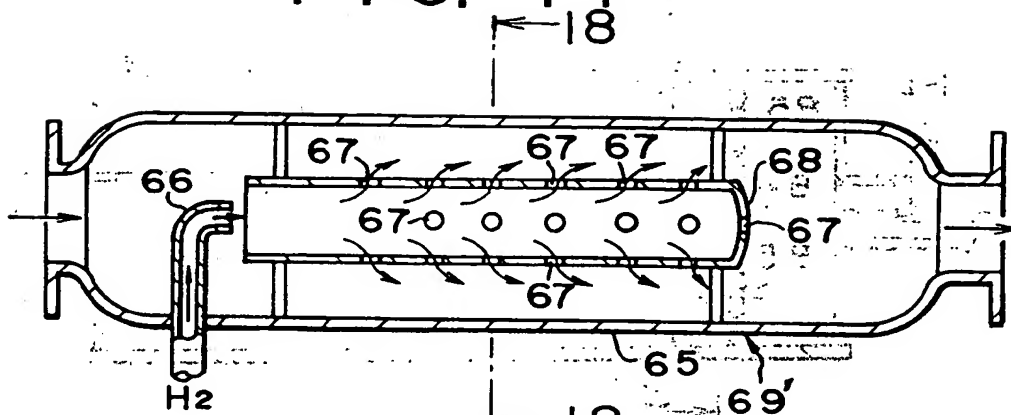


FIG. 18

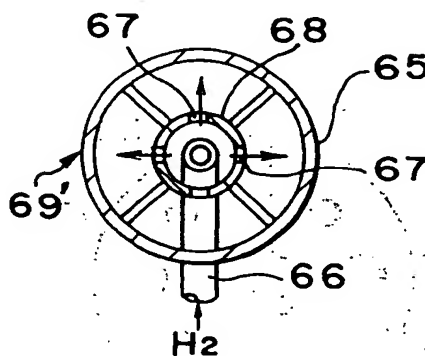
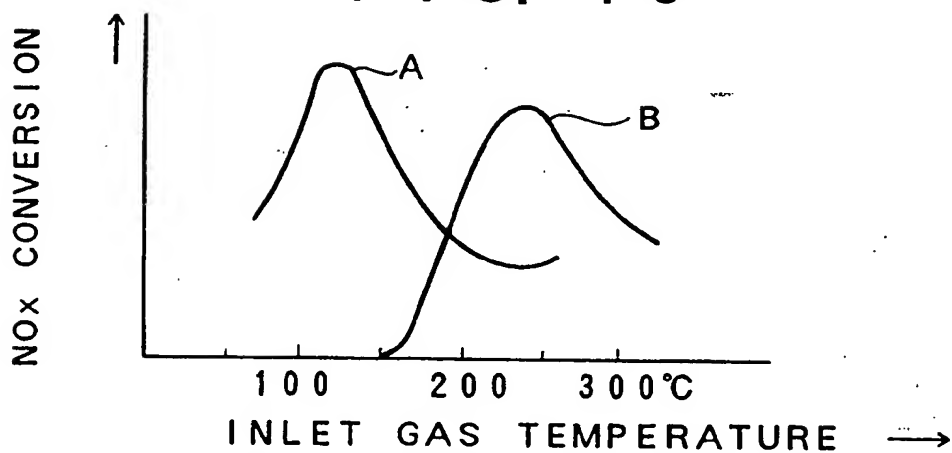


FIG. 19



A: HC, CO REMOVED

B: HC, CO EXIST

CATALYST: MONOLITH, PT/ALUMINA



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 9288

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 147 751 (SUD-CHEMIE AG) * page 11; claims 1-4,6-9; figure *	1-4,12	B01D53/36
A	DATABASE WPIL Derwent Publications Ltd., London, GB; AN 81-449920 & JP-A-56 048 252 (MITSUBISHI HEAVY IND K.K.) 1 May 1981 * abstract *	3-6,8	
A	EP-A-0 380 143 (NIPPON KOKAN K.K.) * claim; figure 1 *	1,10,11	
A	EP-A-0 445 408 (BAYER AG) * the whole document *	1,2, 11-15, 18,25	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B01D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26 JANUARY 1993	Examiner CUBAS ALCARAZ J.L.
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